



THE AQUEOUS CHLORINATION OF BIPHENYL - POSSIBILITIES FOR PCB PRODUCTION IN SEWAGE TREATMENT PLANTS

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THE AQUEOUS CHLORINATION OF BIPHENYL -
POSSIBILITIES FOR PCB PRODUCTION IN SEWAGE
TREATMENT PLANTS

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ABSTRACT

A series of experiments have confirmed that polychlorinated biphenyls (PCBs) may be formed by aqueous chlorination. Under conditions chosen to simulate those encountered in Sewage Treatment Plants, however, it appears that this process is very slow suggesting that the mechanism for PCB formation, while feasible, is not likely to be significant.

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INTRODUCTION

An initial report by Gaffney (1) that disinfection of water by chlorination might produce chlorinated biphenyls from any biphenyl present, was received with scepticism. The chlorination of aromatic compounds is generally accomplished under anhydrous conditions using a Friedel-Crafts catalyst, and direct aqueous chlorination was not considered feasible. Further experimentation by Gaffney (2) and others (3-5) indicated that this process could indeed occur and that, in addition to biphenyl, some ten aromatic organics could be chlorinated.

Biphenyl is widely used as a fungicide in the packing industry, as a dye carrier in textile manufacture and is frequently found in textile plant effluents. As a result concern was expressed that biphenyl might be entering sewage treatment plants (STPs) where polychlorobiphenyls (PCBs) might be formed upon disinfection. Partial support for this hypothesis was found in an earlier study of PCBs in STPs where, in some cases, levels were higher in effluents than in influents (6). The situation in STPs is, however, far more complex than in a laboratory experiment. The mixture, amongst many other components, of ammonia, various ionic species and other organics suggests that chlorination of biphenyl is likely to be even less favourable. Nevertheless, no data was available on biphenyl chlorination under simulated STP conditions.

Consequently a series of experiments was performed to obtain further data. An initial experiment using 2 mg of biphenyl in a saturated aqueous solution of chlorine demonstrated that chlorination did occur and that the products were PCBs. At this point a more detailed study, particularly of the chlorination kinetics, was initiated.

EXPERIMENTAL

a) Preparation of Chlorine Stock Solution

Saturated aqueous chlorine solutions were prepared by bubbling 99.5% pure chlorine gas through 500 ml of organic free water. Chlorine concentrations were determined by iodometric titration to starch/potassium iodide end points, and were generally in the range 6000-6500 ppm. Initially, chlorine solutions were re-saturated as necessary but it was found that this procedure led to accumulation of bromine impurities, with resulting bromination of biphenyl. Thereafter chlorine stock solutions were diluted as necessary and used immediately after preparation.

b) Biphenyl Stock Solutions

Aqueous biphenyl solutions were prepared by adding 10 mg biphenyl (British Drug Houses) to 1 litre of organic free water in a conical flask. The mixture was heated to 85°C, with magnetic stirring, maintained at that temperature for 10 minutes, allowed to stand overnight and filtered twice through a glass-fibre filter. Aliquots of the solution were extracted with hexane for quantitation by comparison of the GC peak height with standard solutions of biphenyl in hexane. Solutions were diluted with organic free water as required.

c) Chlorination Procedure

Biphenyl and chlorine stock solutions were combined to yield mixtures containing 5-6 ppm biphenyl and 6, 60 and 600 ppm chlorine. The two higher chlorine concentration samples were made up to a total volume of 10 ml in 13 ml culture tubes fitted with Teflon-lined screw caps. The lowest chlorine concentration mixtures were prepared to a total volume of 25 ml in 25 ml volumetric flasks.

The reaction mixtures were allowed to stand for various periods at room temperature, following which the reactions were quenched by the addition of a few drops of saturated sodium thiosulphate solution. 1 ml of hexane was added to extract the organics and the aqueous layer removed by suction. The organic layer was diluted to 5 ml with hexane. A drop of metallic mercury was added, the tube capped and placed in an ultrasonic bath to remove any free sulphur formed by reaction between sodium thiosulphate and chlorine.

d) Analytical Method

Quantitative analyses were performed by Gas Chromatography. After some initial experimentation a mixed phase column consisting of 1.5% SP-2250 and 1.95% SP-2401 on 100/120 mesh Supelcoport AW-DMCS was used. Relevant conditions were as follows:

Instrument: Hewlett-Packard 7620A.

Column: 2.6m x 2m id. column. Nitrogen carrier gas at 20 ml/minute.

Detector: ^{63}Ni Electron Capture, in pulsed mode operation, with 95% Argon
5% Methane make-up gas at 40 ml/minute.

Temperature Program: $180^{\circ}\text{-}260^{\circ}\text{C}$ at $4^{\circ}/\text{minute}$.

Peak identification was accomplished by GC/MS analyses, using the same column and conditions as listed above, on an HP7620 interfaced to an AEI (KRATOS/AEI) MS30 double focussing, magnetic sector mass spectrometer.

In studying the affects of reagent concentrations, GC responses were compared. For actual kinetic measurements, however, only biphenyl quantitations were used since this analytical method is unable to separate the isomeric PCBs.

RESULTS

The results of the initial experiment are shown in Figure 1. This experiment was performed using 2 mg of biphenyl in a saturated aqueous solution of chlorine; the reaction was allowed to proceed for one hour. The figure shows the results of a GC/MS analysis of the hexane extract. The top trace is the FID output which is obtained simultaneously with mass spectral analysis. The second trace (TIC) corresponds to the summed intensities of all ions seen by the mass spectrometer and reproduces the FID trace fairly closely. The remaining traces represent the individual intensities of various ions chosen to indicate the presence of biphenyl with 0, 1, 2, 3 or 4 chlorine atoms. A peak in one of these latter traces usually indicates the presence of the corresponding PCB in the FID peak. In some cases two of the traces peak together and this arises from the fragmentation of the heavier compound, generally by loss of one or more chlorine atoms, to give an ion which corresponds to the lighter compound. Analyses of this kind permit peaks in the GC trace to be identified, as has been performed for the upper trace. The results indicate that with a concentrated chlorine solution, PCBs containing up to four chlorine atoms are formed readily.

The effect of chlorine concentration was investigated by comparing several variables (biphenyl remaining, total number of GC peaks, etc.) in solutions incubated for 21 days with chlorine solutions of various strengths. Figure 2 is a histogram of the concentration of biphenyl remaining as a function of the initial chlorine concentration: all solutions were initially 6 ppm biphenyl. The solutions behave much as expected and the biphenyl is completely consumed in mixtures initially 60 and 600 ppm in chlorine. Figure 3 is a histogram of the number of GC peaks detected by electron capture detector at the end of the 21 day period. It shows that the product distribution changed with chlorine concentration and that the

GC-MS; 2mg biphenyl in 1l. sat'd chlorine solⁿ
(1 hour; hexane extract)

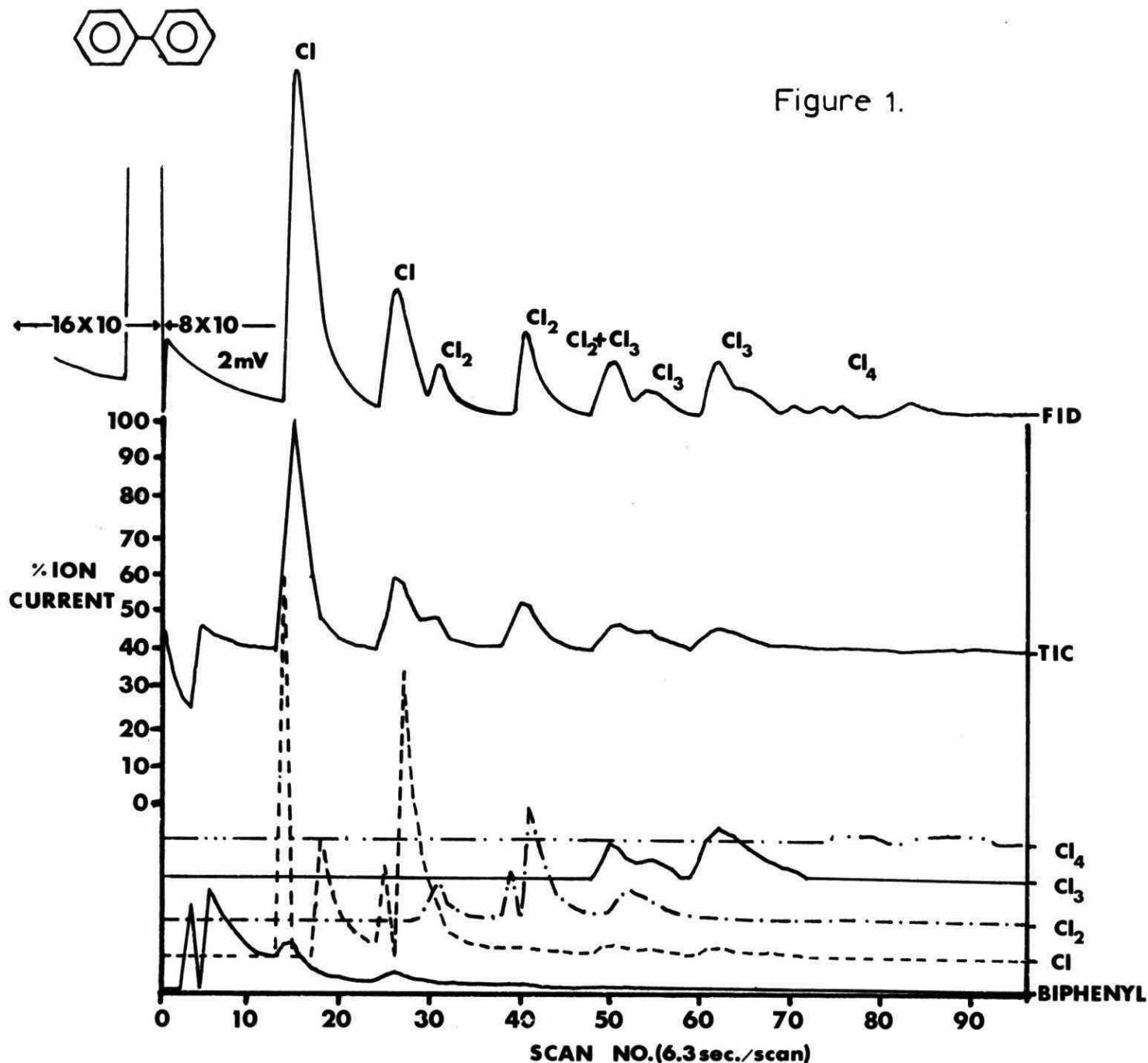


Figure 2.

BIPHENYL REMAINING AFTER Cl_2 INCUBATION

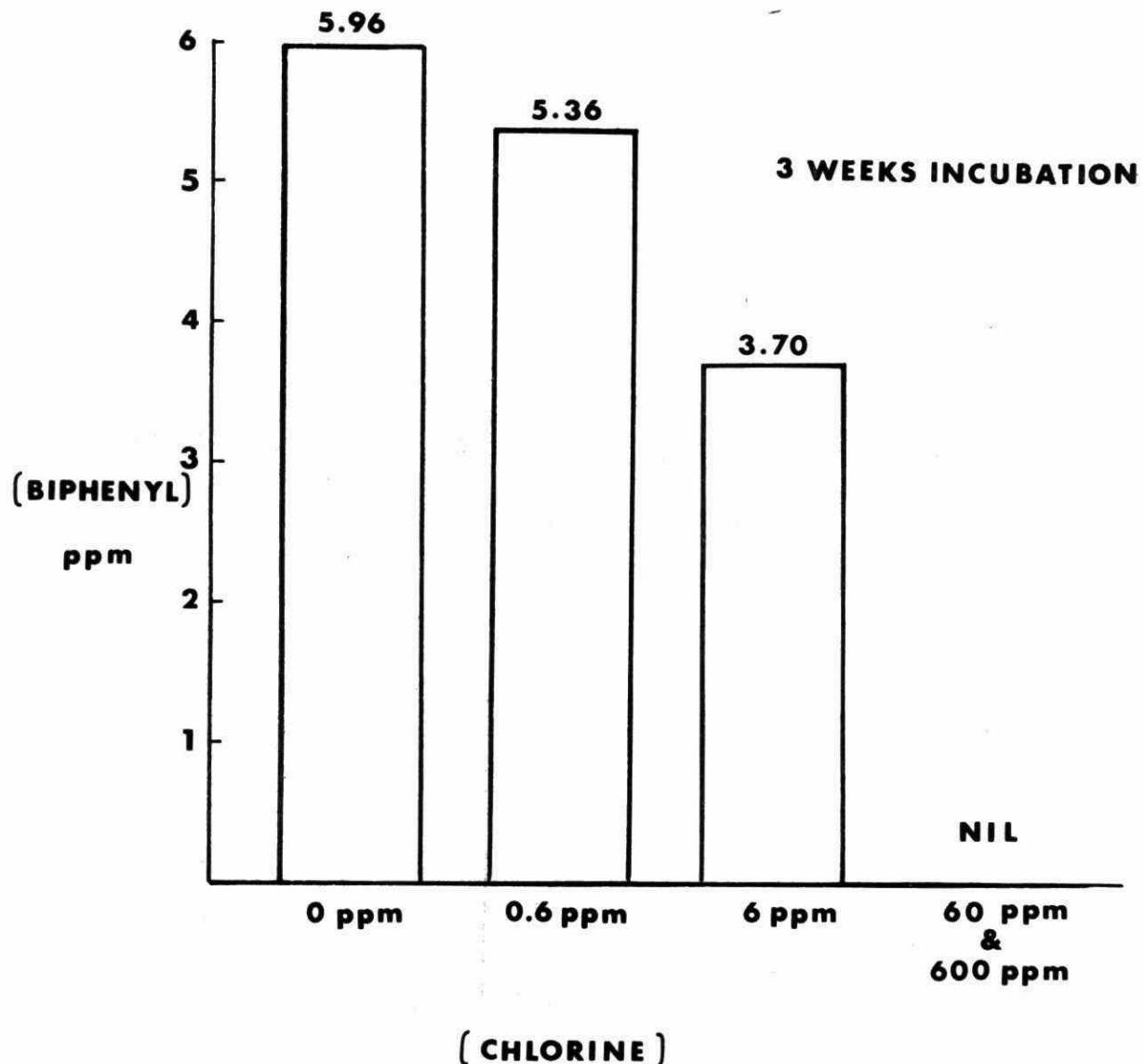
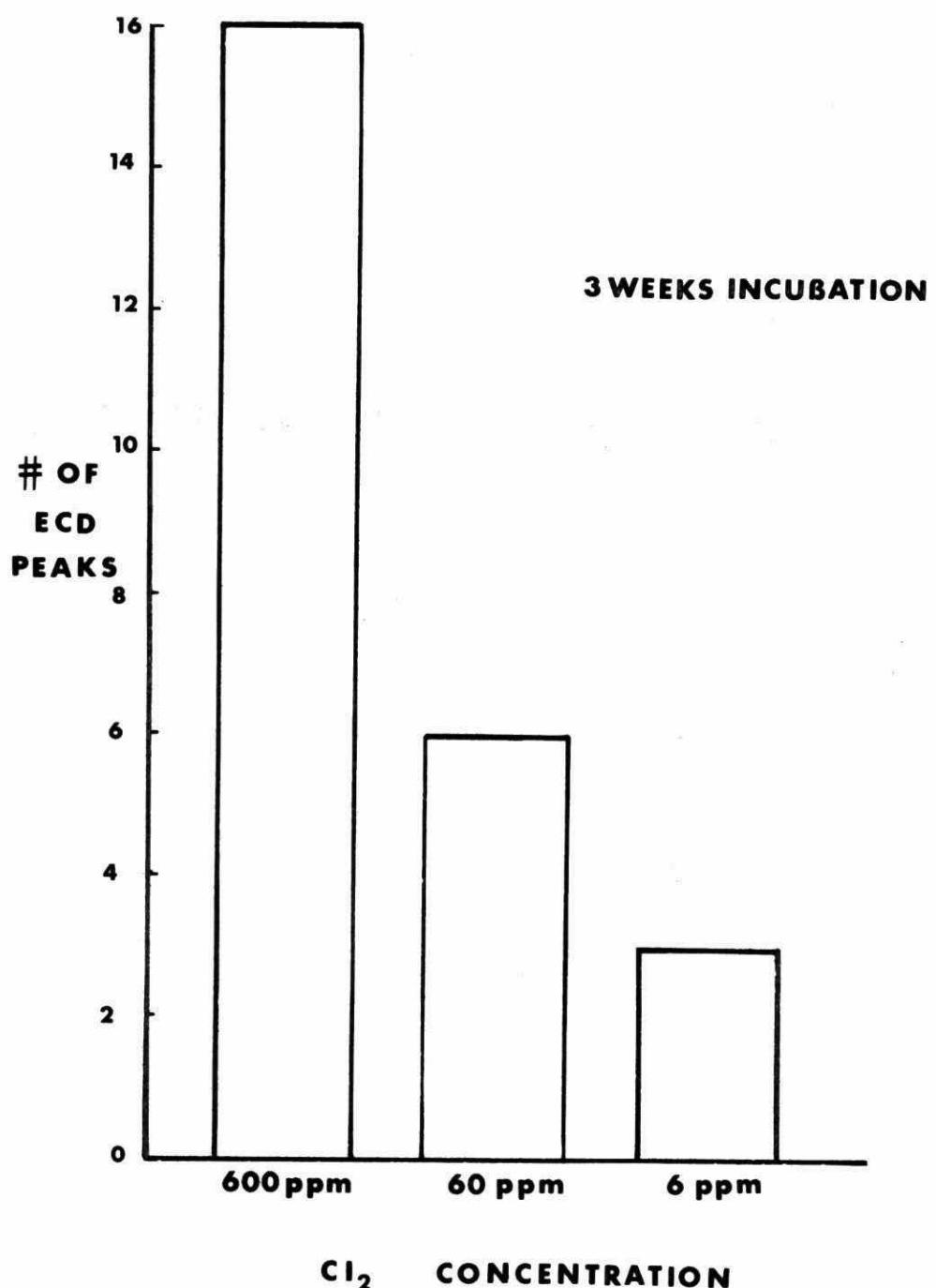


Figure 3.

NUMBER OF PCB PEAKS DETECTED

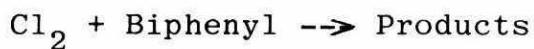
GC-COL.: 1.5% SP-2250 / 1.95% SP-2401; 8ft.



number of PCBs increases with chlorine concentrations:
This is also illustrated by Figure 4 which shows the summed height
of the GC peaks attributed to PCBs.

The distribution of PCB peaks obtained with 600 ppm chlorine
at the end of 21 days is compared with a standard Aroclor
sample in Figure 5. The chromatograms are reasonably similar,
although there are obvious differences, which is rather
surprising since the sample obtained in this work was produced
under aqueous conditions, while the Aroclors are produced by
anhydrous chlorination with an aluminum chloride ($AlCl_3$)
catalyst followed by fractionation. The major differences
between the two traces is the intensity of particular peaks.
Clearly production of certain PCBs is favoured in one procedure
and it may be that unusual isomers are produced by aqueous
chlorination. This is an interesting possibility, but one
that requires far more sophisticated GC for elucidation.

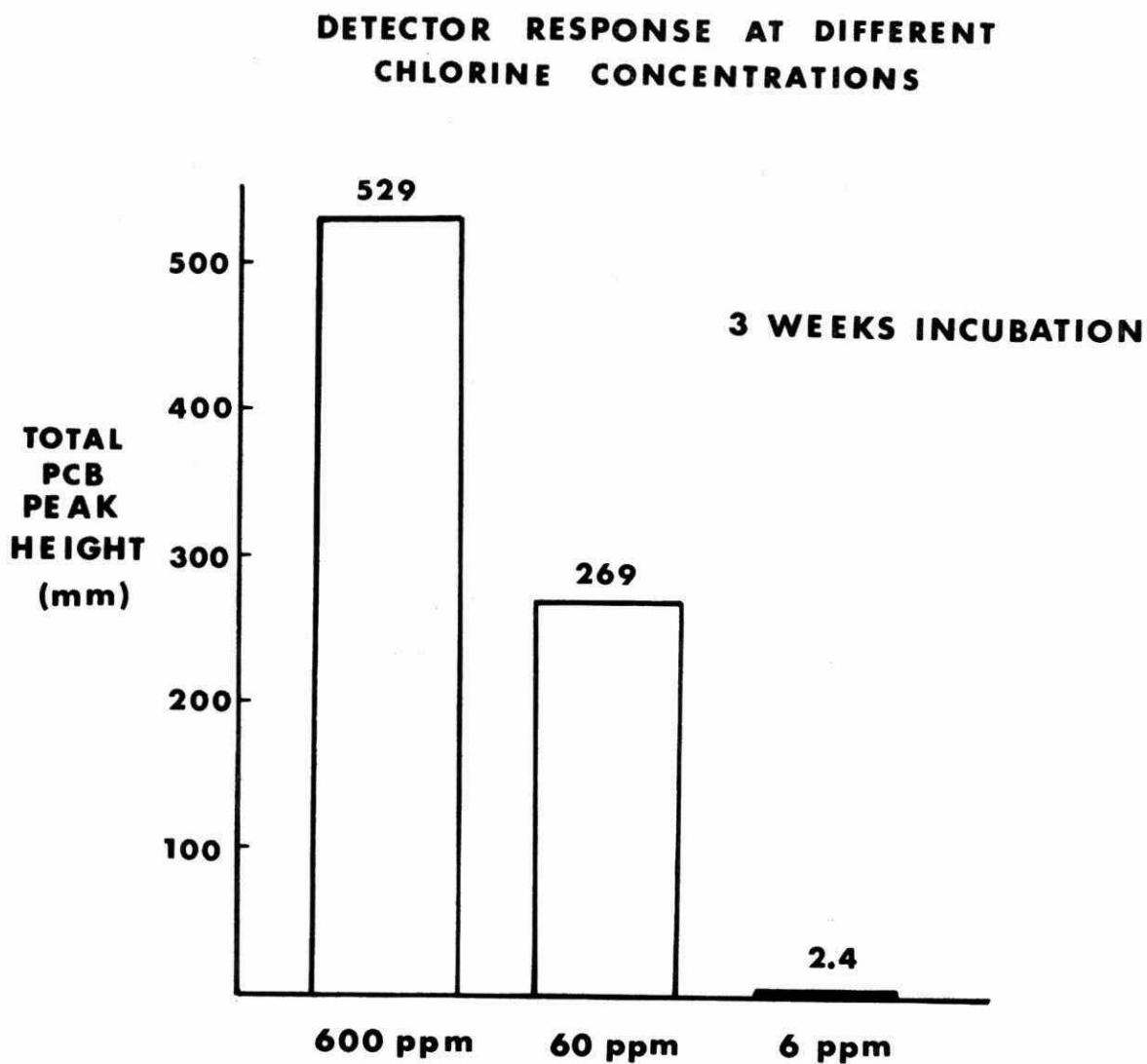
The concentration of biphenyl remaining at various times after
mixing a 5.4 ppm biphenyl solution with 60 ppm chlorine is
shown in Figure 6. The exponential decay demonstrates that
the reaction:



is pseudo first order under these conditions, that is the
concentration of chlorine may be taken as a constant, and
that the half-life of biphenyl is of the order of two hours.
In other words the reaction is reasonably fast and might indeed
constitute a source of PCBs on chlorination processes, if
other effects are absent.

To simulate the conditions of a STP a slightly different
procedure was used. Generally chlorine concentrations in the
order of 15-30 ppm are used for disinfection and consequently
concentrations of 6 ppm and 18 ppm were used in this study.
Measured biphenyl concentrations in STP input streams are
generally lower than 1 ppm and hence the stock solutions were

Figure 4.



COMPARISON OF SAMPLE WITH PCB STD.

Figure 5.

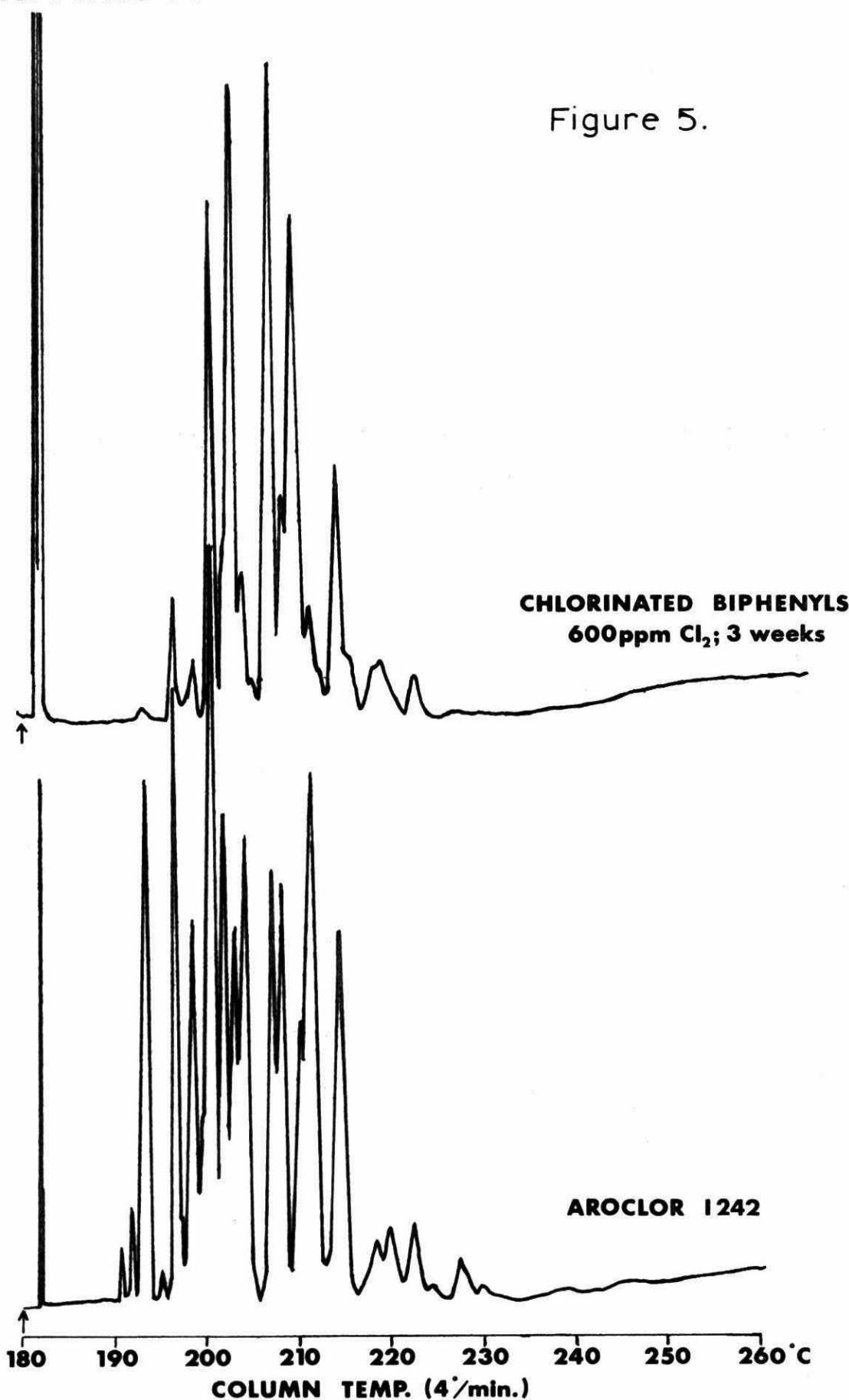
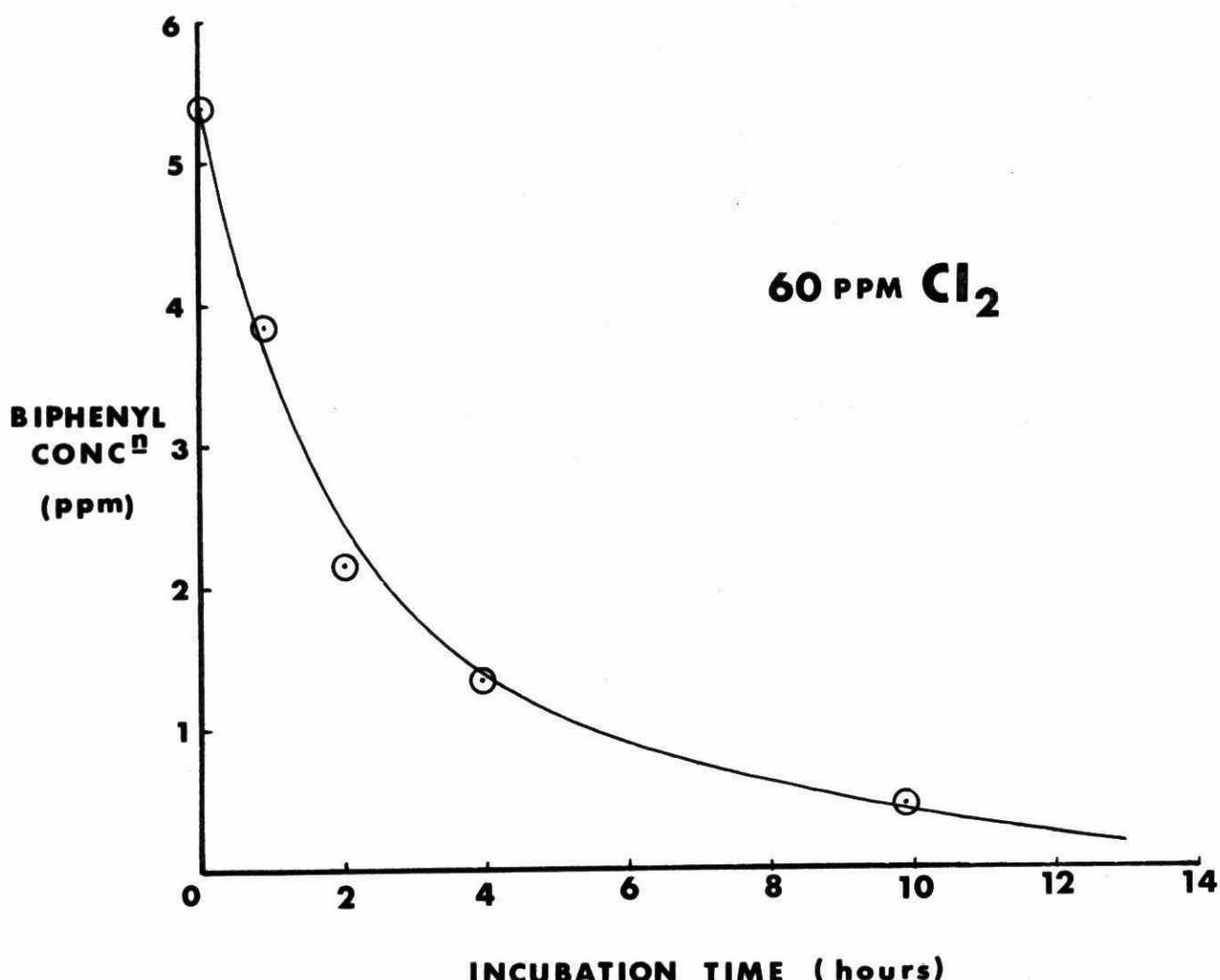


Figure 6.

BIPHENYL CONCENTRATION vs TIME



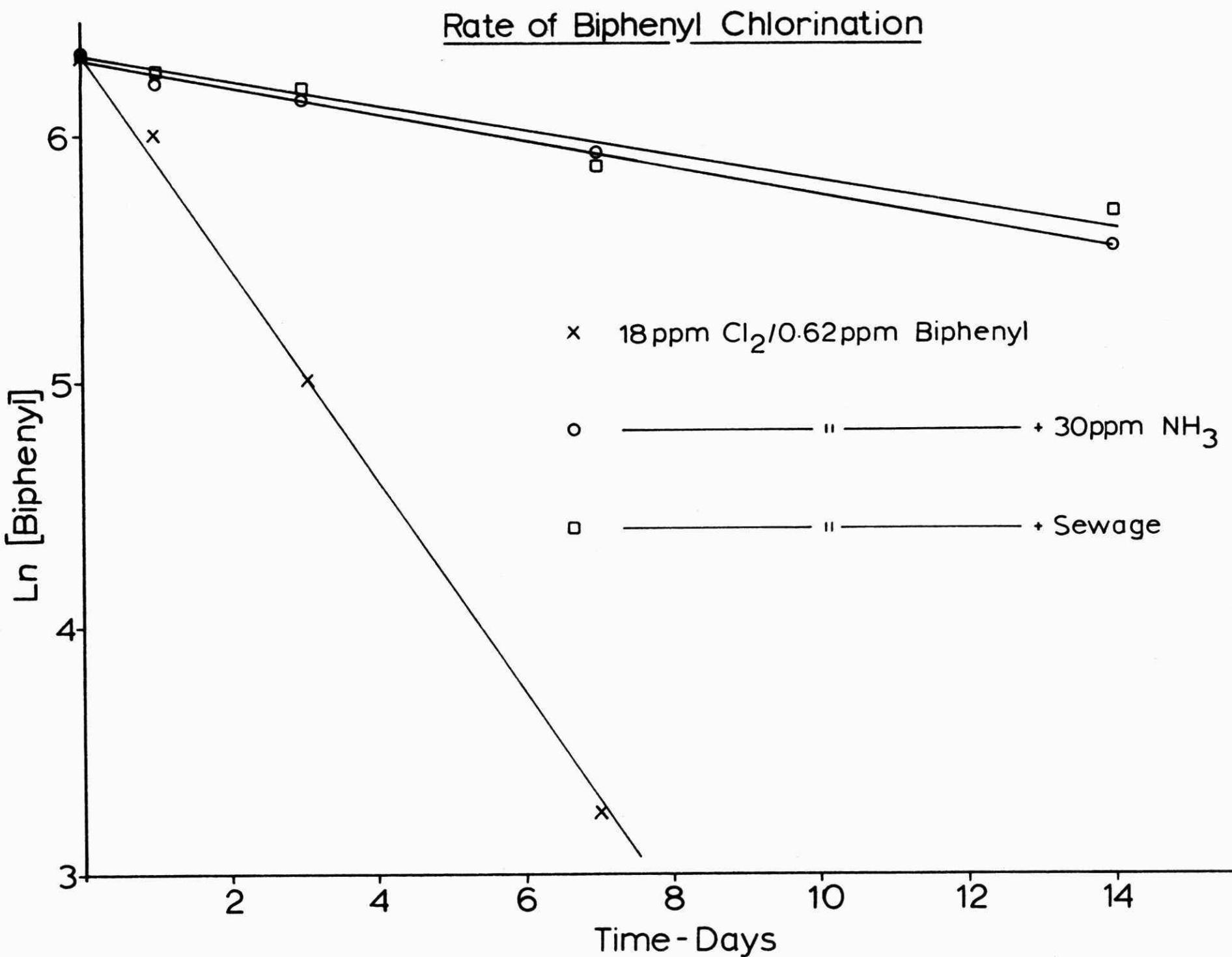
diluted to yield 0.62 ppm in the reaction mixtures. Raw and primary sewage samples were combined and the mixture found to contain 33 ppm free ammonia and 33-37 ppm total Kjeldahl nitrogen. To simulate the ammonia concentrated NH_4OH solutions were diluted appropriately to yield 30 ppm ammonia.

The results of these experiments are reproduced in Figures 7 (18 ppm chlorine) and 8 (6 ppm chlorine). These Figures are plots of the natural logarithm of the biphenyl concentration remaining at various times from the start of the reaction vs. the time, and should be straight lines for first order reactions.

Referring to Figure 7, the steepest line (i.e. the most rapid reaction of biphenyl) corresponds to the system containing only biphenyl and chlorine. When sewage or ammonia are added to the reaction mixture the rate of reaction drops dramatically by almost a factor of ten. Similar results are depicted in Figure 8 for the lower chlorine concentration. The results for biphenyl and chlorine alone show a less steep slope than those in Figure 7 which is to be expected since the chlorine concentration has been reduced, but the results for the solution containing ammonia are very similar for both chlorine concentrations. This latter point demonstrates that the cause of the reduced reaction rate is that the chlorine is consumed by the ammonia and hence the chlorine concentration, and not the biphenyl concentration, becomes the limiting factor. Presumably, since the curves for ammonia and sewage are almost identical, ammonia or amino compounds are the major cause of this reduction in the system containing sewage.

CONCLUSION

The feasibility of the aqueous chlorination of biphenyl has been confirmed: biphenyl can, indeed, be chlorinated under these conditions and the products formed are chlorinated biphenyls. The reaction is surprisingly fast if no other materials are present.



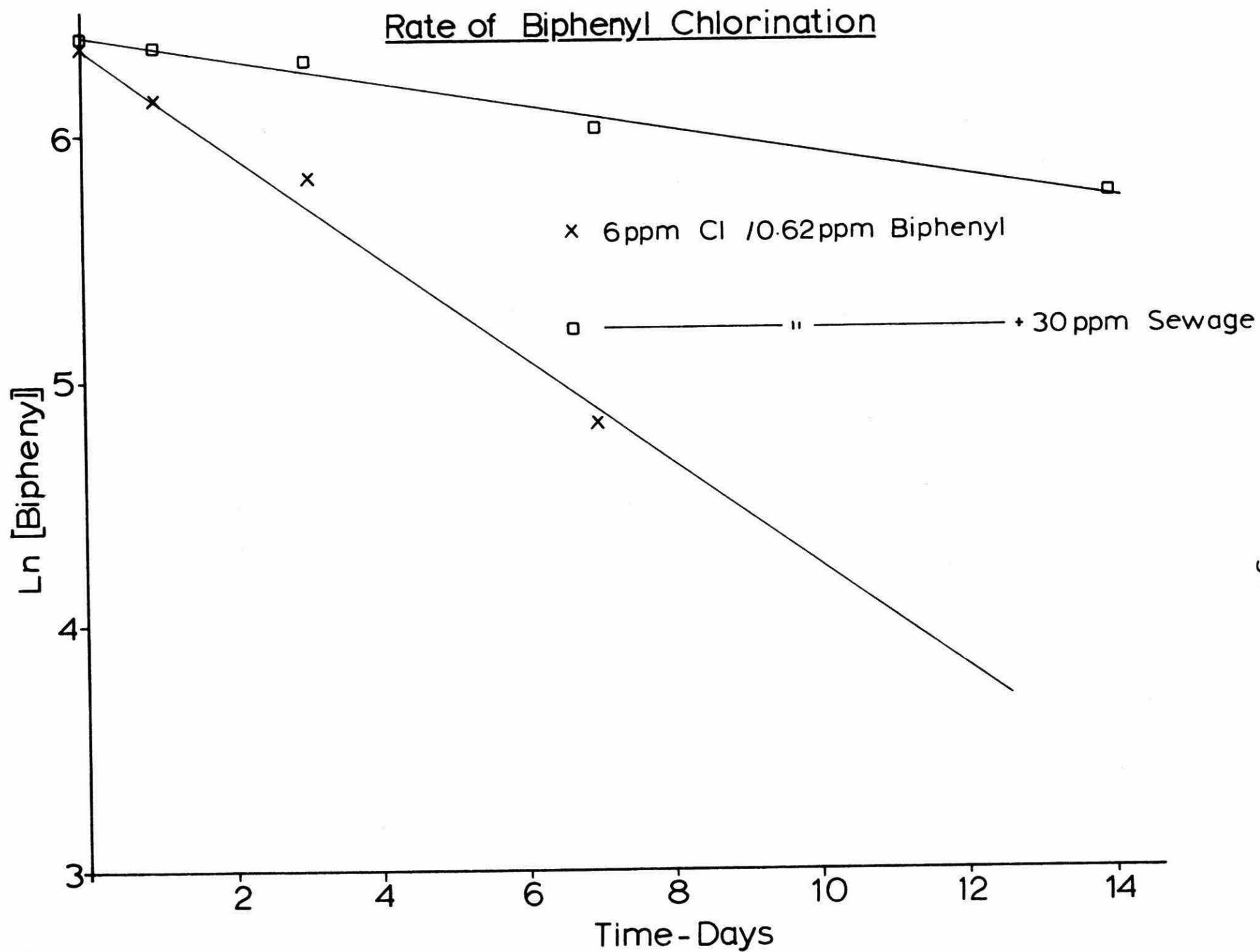


Figure 8.

Under conditions chosen to simulate actual conditions of sewage treatment, however, the reaction rate is considerably slowed. Ammonia or amino compounds appear to be the major cause of this phenomenon and presumably act by reducing the concentration of available free chlorine.

Since the conditions normally used for disinfection in STPs involve initial chlorine concentrations of 15-30 ppm and contact times of one hour or less, it is highly unlikely that chlorination is a significant source of PCBs. From Figure 7 it can be estimated that the percentage loss of biphenyl in one hour at 18 ppm chlorine is 0.37%; a minute change. It should also be remembered that only the ammonia concentration has been simulated: the actual situation in a STP is far more complex and the presence of additional components can only reduce the chlorination rate of biphenyl still further.

The earlier report (6) in which PCB levels were, in some cases, found to be higher in effluents from STPs than in input streams, probably arises from local variations, time differences and inhomogeneities. Input concentrations to such plants are known to vary over quite wide ranges, and it is clearly impossible to guarantee that samples are taken from the same portion of the two streams. The result of this is that it is quite likely that the input and output concentrations are different, but not as a result of the chlorination.

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We wish to thank Messrs. T. Ma and D. Robinson for their assistance with the GC/MS analyses.

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6. Compilation of Data on PCBs in STPs collected by Pesticides Section, reproduced in Appendix 1.

APPENDIX 1

**PCB MONITORING RESULTS FOR
SEWAGE TREATMENT PLANTS
IN ONTARIO.**

DETECTION LIMIT 0.01 ppb

LOCATION	DATE	INFLUENT (ppb)	EFFLUENT (ppb)
<u>THUNDER BAY</u>			
North	Mar. 26, 74	0.780	0.350
South	Mar. 26, 74	0.230	0.240
Northward	Dec. 18, 74	0.110	0.140
Southward	Dec. 18, 74	0.600	0.140
Northward	Apr. 15, 75	0.190	0.280
Southward	Apr. 15, 75	0.180	0.180
Fort William STP	July 29, 75	-	0.250 Treated Sewage
Port Arthur STP	July 29, 75	-	0.250 Treated Sewage
Intercity Ditch	July 29, 75	-	Non-detectable surf. water
Port Arthur McVicar Cr.	July 29, 75	-	Non-detectable storm sewer
Fort William Neebing R.	July 29, 75	-	Non-detectable storm sewer
Great Lake Paper Co.	July 29, 75	-	Non-detectable
<u>NIPIGON</u>			
STP	Dec. 7, 73	0.120	0.360
	Mar. 26, 74	0.780	0.580
	July 29, 74	0.170	0.050
	Dec. 17, 74	0.310	0.250
	Apr. 15, 75	0.200	0.100
<u>TERRACE BAY</u>			
West end	Dec. 7, 73	0.710	0.570
East end	Dec. 7, 73	0.250	0.290
West Tank	Mar. 19, 74	0.440	1.100
East Tank	Mar. 19, 74	0.630	-
West Tank	June 29, 74	2.500	0.290
East Tank	June 29, 74	0.460	0.370
West Tank	Dec. 9, 74	0.320	0.120
East Tank	Dec. 9, 74	0.220	0.100
East	Apr. 14, 75	0.160	0.510
<u>MARATHON</u>			
STP	Dec. 7, 73	0.490	0.390
	Mar. 18, 74	1.040	0.330
	Aug. 6, 74	0.320	0.160
	Dec. 3, 74	0.250	0.190
	Apr. 14, 75	0.440	0.210
<u>SAULT STE. MARIE</u>			
STP	Dec. 9, 73	0.320	0.250

LOCATION	DATE	INFLUENT (ppb)	EFFLUENT (ppb)
<u>SUDBURY</u>			
STP	Apr.17,74	0.090	0.136
<u>NORTH BAY</u>			
STP	Apr.17,74	0.370	0.100
<u>PARRY SOUND</u>			
STP	Sept.18,73 Apr.17,74	0.850 0.135	- 0.038
<u>GRAVENHURST</u>			
STP	Apr.17.74 Apr.17,74	0.090 0.200	0.136 0.040
<u>BARRIE</u>			
STP	Apr.17,74	0.390	0.190
<u>MIDLAND</u>			
STP	Apr.17.74	0.190	0.039
<u>COLLINGWOOD</u>			
STP	Sept.19,73 Apr.17,74 Aug.6,74	0.920 0.298 0.350	0.440 0.112 0.130
<u>MEAFORD</u>			
STP	Sept.19,73 Apr.17,74 Aug.26,74 Dec.3,74	4.200 0.950 5.200 non-detectable	2.400 0.260 4.800 non-detectable
<u>OWEN SOUND</u>			
	Sept.18,73 Apr.17,74 Aug.26,74	0.340 0.275 0.200	0.390 0.286 non-detectable
<u>WIARTON</u>			
	Sept.17,74	-	0.015

LOCATION	DATE	INFLUENT (ppb)	EFFLUENT (ppb)
<u>GODERICH</u>			
STP	Sept.18,73	0.290	0.090
	Sept.19,74	0.140	0.050
	Dec.17,74	non-detectable	non-detectable
<u>SARNIA</u>			
(lagoon)			
Polysar pump site	Sept.24,73	trace	trace
STP	July 29,75	non-detectable	non-detectable
<u>WALLACEBURG</u>			
STP	July 16,75	-	non-detectable
<u>WINDSOR</u>			
STP	July 16,75	-	non-detectable
<u>PENETANGUISHENE</u>			
STP	Sept.19,73	0.160	trace
STP	Apr.17.74	non-detectable	0.056
Mental Hospital	Aug.21,74	0.070	non-detectable
STP	Aug.21,74	2.300	0.160

LOCATION	DATE	PCB (in ppb)
Cornwall STP	June 26,75	0.051
	June 26,75	0.052
	June 26,75	0.025
	June 26,75	0.076
Brockville STP	June 26,75	0.077
	June 26,75	0.100
Kingston STP	June 26,75	0.050
	June 26,75	0.051
Bellville STP	June 26,75	non-detectable
	June 26,75	non-detectable
Trenton	June 26,75	0.050
	June 26,75	0.075
Cobourg STP	July 3,75	non-detectable
Welland Canal @ Cobourg	July 3,75	non-detectable
	Aug.11,75	non-detectable
Oshawa STP	July 3,75	non-detectable
	July 3,75	non-detectable
Toronto East STP	July 3,75	non-detectable
	July 3,75	non-detectable
Toronto West STP	July 11,75	0.540 sewage effluent 0.600 sewage effluent
Oakville STP	July 8,75	0.400 sewage effluent
	July 8,75	0.400 sewage effluent
Burlington STP	July 8,75	0.300 sewage effluent
	July 8,75	0.300 sewage effluent
Clarkson STP	July 11,75	non-detectable)sewage
	July 11,75	non-detectable)effluent

LOCATION	DATE	PCB (in ppb)
Hamilton STP	July 8,75 July 8,75	0.100 sewage effluent 0.100 sewage effluent
St. Catherines STP	July 8,75 July 8,75	non-detectable sewage effluent non-detectable sewage effluent
WELLAND (above Patterson Sewer) (Canal)	Sept.10,74	non-detectable
Patterson Sewer	Sept.10,74	non-detectable
Atlas 42 Sewer	Sept.10,74	0.110
Atlas 36 Sewer	Sept.10,74	non-detectable
Guelph (Storm Sewer)	July 10,75 July 10,75	non-detectable 0.250
St. Thomas STP	July 16,75 July 16,75	non-detectable sewage effluent non-detectable
Chatham STP	July 16,75 July 16,75	non-detectable sewage effluent non-detectable
Nanticoke (Generating Station)	July 16,75 July 16,75	non-detectable cooling water non-detectable cooling water
Lakeview (Generating Station)	July 16,75 July 16,75	non-detectable cooling water non-detectable cooling water

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